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(54) POROUS HONEYCOMB STRUCTURAL BODY, APPLICATION THEREOF AND MANUFACTURING METHOD THEREFOR

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a porous honeycomb structural body capable of simultaneously satisfying both characteristics of pressure loss and isostatic strength which are incompatible with each other, and to provide a manufacturing method therefor.

SOLUTION: In the porous honeycomb structural body containing cordierite as a main crystal phase and provided with a partition wall having 40 to 75% porosity and 10 to 50 μm average pore diameter, the porosity and the pore diameter in the center part is made larger than that of the outer peripheral part.

* NOTICES *

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CLAIMS

[Claim(s)]
[Claim 1]They are 40 to 75% of porosity which makes cordierite a main crystal phase, and a porosity honeycomb structured body provided with a septum with an average pore diameter of 10-50 micrometers, A porosity honeycomb structured body, wherein porosity and a pore diameter in the central part of this honeycomb structured body are larger than porosity and a pore diameter in the peripheral part.
[Claim 2]A pore diameter [in / it is large not less than 2%, and / the central part of this honeycomb structured body] of porosity in the central part of said honeycomb structured body is the porosity honeycomb structured body according to claim 1 large not less than 2 micrometers to a pore diameter in this the peripheral part to porosity in said the peripheral part.

[Claim 3]Porosity in the central part of said honeycomb structured body is the porosity honeycomb structured body according to claim 1 or 2 large not less than 3% to porosity in said the peripheral part.
[Claim 4]A pore diameter in the central part of this honeycomb structured body is the porosity honeycomb structured body according to any one of claims 1 to 3 large not less than 3 micrometers to a pore diameter in this the peripheral part.
[Claim 5]A filter of the porosity honeycomb structured body according to any one of claims 1 to 4, or directions for use as catalyst support.
[Claim 6]Use a cordierite-ized raw material as the main raw material, and a Plastic solid of honeycomb structure is produced using a plastic matter which contains five or more mass parts of carbon to this cordierite-ized raw material 100 mass part at least, It is a manufacturing method of a porosity honeycomb structured body which dries this Plastic solid and is calcinated, A manufacturing method of a porosity honeycomb structured body carrying out temperature up of the ambient temperature at speed at which carbon which exists in the

central part of this Plastic solid is burned down by Plastic solid central part not less than 1200 ** temperature of less than 1430 ** when calcinating this Plastic solid.

[Claim 7]A manufacturing method of the porosity honeycomb structured body according to claim 6 which carries out temperature up of said ambient temperature at the rate of 20-60 ** / hr in a 400-1150 ** temperature requirement.

[Claim 8]A manufacturing method of the porosity honeycomb structured body according to claim 6 or 7 which holds said ambient temperature in the temperature requirement in a 1150-1200 ** temperature requirement for 5 hours or more.

[Claim 9]A manufacturing method of the porosity honeycomb structured body according to any one of claims 6 to 8 using a plastic matter which contains said carbon by 25 or less mass parts to said cordierite-ized raw material 100 mass part.

[Claim 10]A manufacturing method of the porosity honeycomb structured body according to any one of claims 6 to 9 whose atmosphere at the time of calcinating said Plastic solid is seven to oxygen density 17 volume % in 400-1150 ** ambient temperature.

[Claim 11]A manufacturing method of the porosity honeycomb structured body according to any one of claims 6 to 10 using a plastic matter which contains foamed resin by less than five mass parts to said cordierite-ized raw material 100 mass part.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to a porosity honeycomb structured body, its use, and a manufacturing method for the same. It is related with a porosity honeycomb structured body which reduced pressure loss, and a manufacturing method for the same, controlling distribution of porosity and a pore diameter and maintaining isostatic intensity in more detail. The porosity honeycomb structured body of this invention can be especially used preferably as the filter for emission gas purification, and catalyst support.
[0002]
[Description of the Prior Art]A close-up of the influence of the environment on car motor, the particulate matter especially discharged from a diesel power plant etc., or NOx is taken greatly these days, and use of the porosity honeycomb structured body is variously considered as an important means to remove such a toxic substance.
[0003]For example, in the honeycomb structured body which has two or more breakthroughs divided by the porous septum, The honeycomb filter which catches the particulate matter in exhaust gas and is removed is developed by considering it as the structure which ******(ed) in a mutually different position in respect of the both ends which a breakthrough punctures, making exhaust gas flow into each breakthrough which carries out an opening to the end face of 1, and passing the septum in a honeycomb structured body compulsorily. Development is furthered also for the catalyst body of the honeycomb structure which made the catalyst which decomposes all the septa as a new trial which raises purification performance, and decomposes HC and NOx as a porous body of high porosity support by increasing a catalyst holding amount.
[0004]On the other hand, although such a porosity honeycomb structured body is grasped by metal casing etc. via grasping material in the case of use, In order to grasp by fixed thrust so

that a gap may not take place to metal casing and a honeycomb structured body even if it receives the continuous vibration from an engine etc., the isostatic intensity which can bear this is required. Low fuel consumption, the request of pressure loss reduction from the point of a high increase in power if it is in recent years especially, Or the necessity of securing sufficient isostatic intensity is pointed out strongly, high porosity-ization of a honeycomb structured body progressing and filling the request of this raise in porosity from the request of the catalyst holding amount increase from the point of improvement in exhaust gas purification performance. If it is in the porosity honeycomb structured body installed in an exhaust gas course, By the center portion of a channel, the flow of exhaust gas increases and the ease of flowing and HC of exhaust gas in the center portion of the honeycomb structured body concerned, and the amount of NOx decomposition, Since whole pressure loss and purification performance are influenced greatly, the filter and catalyst body of structure which corresponded to the difference of flow distribution of such exhaust gas exactly are desired.

[0005]On the other hand, as a conventional porosity honeycomb structured body, "The porosity is not less than 45% of 60% or less, and pore volume ratios with the aperture of not less than 100 micrometers are 10% or less of total pore volume ratios, and toward an inside from the surface The specific surface area (Mm^2/g) of an opening and all the stomata to penetrate, by having composition so that the relation to range" of 1000M+85N >=530 with the surface roughness (Nmum) in the filter surface may become, the honeycomb structured body which catching time can be [honeycomb structured body] long and can decrease reproduction frequency is indicated (patent documents 1).

[0006]By supposing "the pore volume ratio of porosity 2 micrometers or less in diameter is 0.015 or less cc/g at not less than 40% of 55% or less", even if it is the same collection efficiency and a pressure loss, the porosity ceramic honeycomb structured body to which catching time becomes long substantially is indicated (patent documents 2).

[0007]The coefficient of thermal expansion between "25-800 ** Below $0.3x10^{-6}$/**. By porosity's being 55 to 80%, and an average pore diameter's being 25-40 micrometers, and the stoma of a partition surface consisting of a 5-40 micrometers stoma and a 40-100-micrometer osculum, and making the number of the above-mentioned stomata into five to 40 time" of the number of the above-mentioned osculums, The cordierite honeycomb structured body having the characteristic of high collection efficiency, low pressure loss, and the rate of low thermal expansion is indicated (patent documents 3).

[0008]

[Patent documents 1] The patent No. 2726616 gazette [Patent documents 2] The patent No. 2578176 gazette [Patent documents 3] JP,9-77573,A[0009]However, each of these honeycomb structured bodies controlled pore distribution, and was not taken into consideration at all about the point of satisfying simultaneously the opposite characteristic of reduction of

pressure loss, increase of a catalyst holding amount, and reservation of isostatic intensity.
[0010]
[Problem(s) to be Solved by the Invention]This invention is made in view of an above-mentioned problem, and is a thing.
The purpose can satisfy the opposite characteristic of isostatic intensity simultaneously, It is providing a honeycomb structured body usable as a catalyst body which decomposes HC, NOx, etc. in the filter which catches the particulate matter in the suitable porosity honeycomb structured body for the diesel-particulate filter especially installed by the combustion engine, for example, exhaust gas, and is removed, or exhaust gas, and is removed, and a manufacturing method for the same.

[0011]
[Means for Solving the Problem]As a result of this invention person's inquiring wholeheartedly in order to solve an above-mentioned technical problem, when calcinating first a Plastic solid of honeycomb structure which uses a cordierite-ized raw material as the main ingredients, At temperature (temperature of goods) of a 1000-1200 ** Plastic solid, although firing shrinkage of a Plastic solid was remarkable, it found out a phenomenon in which firing shrinkage hardly arose, out of this temperature requirement. and carbon which this invention person repeats research further and exists in the central part of a Plastic solid using carbon as ostomy material -- temperature of the central part of a Plastic solid -- an account of the upper -- so that it may not be burned down until it exceeds this temperature requirement, By controlling a heating rate of a firing environments, by a center portion which influences reduction of pressure loss greatly, a pore diameter and porosity acquire knowledge that a big honeycomb structured body can be obtained, and came to complete this invention.
[0012]Namely, 40 to 75% of porosity which makes cordierite a main crystal phase according to this invention, And it is a porosity honeycomb structured body provided with a septum with an average pore diameter of 10-50 micrometers, and a porosity honeycomb structured body, wherein porosity and a pore diameter in the central part of the honeycomb structured body concerned are larger than porosity and a pore diameter in the peripheral part is provided. The "central part" means a septum portion in a position nearest to the medial-axis middle point or the middle point concerned of a honeycomb structured body or a Plastic solid among this specification here, and with a "peripheral part." From the medial-axis middle point of a honeycomb structured body or a Plastic solid, a septum portion to the medial axis concerned perpendicular and located in the periphery side most is meant. Although a honeycomb structured body of this invention specifies porosity and a pore diameter about the "central part", a field where porosity and a pore diameter are bigger than a peripheral part has fixed breadth from the central part. Especially in this specification, it removes, in case there is a

notice, and porosity and a pore diameter mean average porosity and an average pore diameter, respectively.

[0013]In this invention, it is preferred that porosity in the central part of a honeycomb structured body is large not less than 2% to porosity in a peripheral part of a honeycomb structured body, and a thing large not less than 3% is more preferred. It is preferred that a pore diameter in the central part of a honeycomb structured body is large not less than 2 micrometers to a pore diameter in a peripheral part of a honeycomb structured body, and a thing large not less than 3 micrometers is more preferred.

[0014]According to this invention, use a cordierite-ized raw material as the main raw material, and at least carbon, A Plastic solid of a honeycomb structured body is produced using a plastic matter contained five or more mass parts to cordierite-ized raw material 100 mass part, It is a manufacturing method of a porosity honeycomb structured body which dries an acquired Plastic solid and is calcinated, When calcinating the Plastic solid concerned, a manufacturing method of a porosity honeycomb structured body carrying out temperature up of the ambient temperature at speed at which carbon which exists in the central part of a Plastic solid is burned down within the limits of Plastic solid central part not less than 1200 ** temperature [less than 1430 **] is provided.

[0015]In this invention, although it changes also with kinds of carbon using ambient temperature, it is usually preferred to carry out temperature up of the 400-1150 ** temperature requirement at the rate of 20-60 ** / hr.

[0016]After ambient temperature reaches 1150 **, it is preferred to hold in the temperature requirement to a 1150-1200 ** temperature requirement for 5 hours or more.

[0017]It is preferred to produce a Plastic solid of honeycomb structure in a manufacturing method of this invention using a plastic matter which contains carbon by 25 or less mass parts to cordierite-ized raw material 100 mass part at least, It is more preferred to produce a Plastic solid of honeycomb structure using a plastic matter which contains foamed resin by less than five mass parts to cordierite-ized raw material 100 mass part. As for a furnace atmosphere at the time of calcinating a Plastic solid, in at least 400-1150 ** ambient temperature, it is preferred to make an oxygen density into 7 - 17 volume %.

[0018]Here, drawing 1 explains relation between a heating rate in the case of a baking process in a manufacturing method of this invention, and stoma formation. Drawing 1 is a baking process in an embodiment of 1 of this invention, it is a graph which shows a firing environments and a temperature-up state of the honeycomb structured body central part, and a solid line shows temperature of the Plastic solid central part among a figure, and a dotted line shows ambient temperature. Temperature of the Plastic solid central part inserts R thermo couple from a breakthrough, is located in the Plastic solid central part, and is measured.

[0019]Carbon which ambient temperature contains as ostomy material in a manufacturing

method of this invention as shown in drawing 1 (in drawing 1.) An example using graphite is shown. If temperature (about 600 ** is equivalent to this temperature in a figure.) which can burn is reached, temperature of the Plastic solid central part will become higher than ambient temperature, but. Combustion of carbon contained as ostomy material starts, and this shows that temperature inside a Plastic solid is rising by it. In a Plastic solid which consists of a cordierite-ized raw material, firing shrinkage becomes the most remarkable although it has not appeared in a graph, if temperature of a Plastic solid amounts to 1000-1200 ** by raising ambient temperature further. Under the present circumstances, if carbon is already burned down and a stoma is formed, reduction of the pore diameter will be carried out by firing shrinkage, but like an example of drawing 1, if carbon still remains, it will be maintained while a pore diameter has been a path of carbon, and will change. If ambient temperature is raised and temperature of a Plastic solid exceeds 1200 **, firing shrinkage about a Plastic solid becomes small, and if carbon is burned down at this time, the substantially same stoma as a path which carbon had from the first will be formed. Therefore, carbon is already burned down before 1000 **, and it becomes a diameter of an osculum from a stoma in which the path carried out reduction. When carbon in a Plastic solid is burned down thoroughly, in the portion (a graph shows the central part.). The time of becoming a peak once at the time of the completion of carbon destruction by fire, and appearing (in drawing 1, it has appeared in a 1200-1300 ** temperature requirement.) actualizes as temperature of a Plastic solid falls rapidly, it results in ambient temperature or temperature not more than it and it is shown by 1200-1300 ** in a figure after that. And if temperature in which such a rapid temperature change appears laps with 1000-1200 ** which becomes the most remarkable [firing shrinkage of a Plastic solid], firing shrinkage will be reinforced and it will keep even in the situation of a calcination piece very much. Then, Plastic solid temperature in case a heating rate of a firing environments is controlled by this invention and carbon of peak temperature mentioned above, i.e., the Plastic solid central part, is burned down is made to become not less than 1200 **, A stoma which continues being the path which carbon had is formed in the central part, avoiding the situation of a calcination piece. Carbon has many which carbon is burned down easily, are burned down by a comparatively low temperature, and form a stoma from a center section including the central part at a peripheral part of a Plastic solid in more nearly aerobic environment. Therefore, by subsequent firing shrinkage, that to which reduction of the path is carried out will increase, and a difference will be produced in porosity and a pore diameter in a center section and a peripheral part.

[0020]

[Embodiment of the Invention]Hereafter, an embodiment of the invention is described concretely.

[0021]1. The porosity honeycomb structured body of porosity honeycomb structured body this

invention, It has a with the porosity of 40 to 75% which makes cordierite a main crystal phase, and an average pore diameter of 10-50 micrometers septum, and the porosity and pore diameter of the septum concerned are the central part of a honeycomb structured body, and are characterized by being larger than the peripheral part.

[0022]While this secures the isostatic intensity of the grade searched for in the case of grasping to a case, reduction of pressure loss and improvement in purification performance can be attained effectively. Namely, since a pore diameter and porosity are smaller than the central part, a peripheral part as the whole structure, Even if it has the same pore diameter, compared with what does not have a difference in the pore diameter in a peripheral part and the central part, isostatic intensity is large, It can be considered as a stronger honeycomb structured body to the shock by the deficit of the peripheral wall by a physical shock until it attaches to a flue gas treatment apparatus, and the vibration after wearing. And though the catalyst holding amount of the central part can be made more and it has the above-mentioned isostatic intensity in the central part with most flows of exhaust gas while being able to reduce pressure loss since a pore diameter and porosity are large, the purification performance as the whole can be raised more.

[0023]In this invention, the porosity of a septum is made into 40 to 75% because increase of pressure loss becomes it remarkable that the porosity of a septum is less than 40%, and reduction of isostatic intensity will become remarkable, if the porosity of a septum exceeds 75% on the other hand. For this reason, in this invention, as for the porosity of the whole septum, it is preferred that it is 50 to 75%, it is more preferred that it is 57 to 70%, and it is preferred that it is especially 65 to 70%.

[0024]It is preferred that are a big point, and the effect of reducing pressure loss is the central part of a honeycomb structured body, and enlarges the porosity of a septum not less than 2% to the peripheral part of a honeycomb structured body in this invention, enlarging not less than 3% is more preferred, and especially the thing enlarged not less than 5% is preferred. That is, as porosity of the central part, it is 68 to 75% more preferably 55 to 73% 52 to 72%. Of course, naturally change of some of above-mentioned porosity of the central part by manufacturing conditions is in tolerance level, if the porosity of the whole septum is within the limits of the above.

[0025]In this invention, although there is no restriction in particular about the mode of change of the porosity from a peripheral part to the central part, it is preferred that porosity is changing from the peripheral part to the central part continuously at the point that thermal shock resistance is large. As for the porosity in this case, it is preferred that the variation of a before [the septum which forms the cell located in one third from a periphery to / from the point of effective reduction of pressure loss / a medial axis of length] occupies not less than 30% of the whole variation, and especially its thing for which not less than 50% of the whole variation

is occupied is preferred.

[0026]It is because reduction of collection efficiency will become remarkable if it, on the other hand, becomes that the average pore diameter of a septum is less than 10 micrometers easy to produce increase of pressure loss at an early stage by blinding of a stoma in this invention that the average pore diameter of the septum was 10-50 micrometers and the average pore diameter of a septum exceeds 50 micrometers on the other hand. For this reason, it is preferred that the average pore diameter of a septum shall be 15-40 micrometers in this invention, it is more preferred to be referred to as 20-35 micrometers, and especially the thing set to 25-30 micrometers is preferred.

[0027]In this invention, the effect of reducing pressure loss is a big point, it is preferred that the pore diameter of a septum is the central part of a honeycomb structured body, and is large not less than 2 micrometers to the peripheral part of a honeycomb structured body, a thing large not less than 3 micrometers is more preferred, and especially a thing large not less than 5 micrometers is preferred. That is, as a pore diameter of the central part, 17-42-micrometer 12-52 micrometers are 25-37 micrometers more preferably. Of course, naturally change of some of above-mentioned pore diameters of the central part by manufacturing conditions is in tolerance level, if the average pore diameter of the whole septum is within the limits of the above.

[0028]In this invention, although there is no restriction in particular about change of the pore diameter from a peripheral part to the central part, it is preferred that the pore diameter is changing from the peripheral part to the central part continuously at the point that thermal shock resistance is large. As for the pore diameter in this case, it is preferred that variation until it forms the cell located in one third from a periphery to [from the field of effective reduction of pressure loss] a medial axis of length occupies not less than 30% of the whole variation, and especially its thing for which not less than 50% of the whole variation is occupied is preferred.

[0029]Next, in this invention, the restriction in particular may not have everything but making the main ingredients of a septum into cordierite, and which things, such as orientation, non-orientation, alpha crystalline substance, and beta crystalline substance, may be sufficient as the cordierite concerned.

[0030]Mullite, zircon, aluminum titanate, clay bond silicon carbide, Other crystal phases, such as zirconia, a spinel, an indialite, Safi Lynn, corundum, or a titania, may be contained, and these crystal phases may be independent one sort, or may contain two or more sorts simultaneously.

[0031]But as for the material which constitutes a septum from a point of improvement in the thermal shock resistance at the time of elevated-temperature use, in this invention, it is preferred that the coefficient of thermal expansion at 40-800 ** is below 1.0×10^{-6}/**.

[0032]In this invention, there may not be any restriction in particular about the shape of a honeycomb structured body, either, for example, any, such as shape where the side of the pillar of a perfect circle or an ellipse, the square pillars whose shape of the end face is polygons, such as a triangle and a rectangular head, these pillars, and a square pillar curved into the character of **, may be sufficient as the shape of the end face. There may not be any restriction in particular about the shape of a breakthrough, either, for example, any, such as a rectangular head, Hitoshi Yasumi's polygon, a perfect circle, or an ellipse, may be sufficient as sectional shape.

[0033]The honeycomb structured body of this invention can be used as a honeycomb filter by considering it as the structure which ******(ed) two or more breakthroughs which carry out an opening to an exhaust gas inflow side edge and an exhaust gas discharge side edge in a mutually different position in respect of both ends. Under the present circumstances, to the material of ****** material, ****** conditions, etc., there is no restriction in particular and it may usually be applied.

[0034]It can also be considered as a monolith honeycomb catalyst object by supporting a catalyst to the septum of the porosity of a honeycomb structured body. As for cell density, when using as catalyst support, it is [the thickness of 6 - 1500 cell / inch^2 (0.9 - 233 cell / cm^2), and a septum] preferred to consider it as the range of 50-2000 micrometers (about 2-79 mil). Although the length of the shaft orientations (exhaust gas flow direction) of a honeycomb carrier changes also with uses, it is usually 100-250 mm preferably 60-300 mm.

[0035]An adsorption layer may be provided in this honeycomb carrier, and the alumina which has high specific surface area, and the thing which uses zeolite as the main ingredients are usually suitably used for it. Although any of a natural article and synthetic compounds may be sufficient as zeolite and a kind in particular is not limited, it is heat resistance, endurance, and a hydrophobic point, and 40 or more things are suitably used for a Si/aluminum ratio. Specifically, ZSM-5, USY, beta-zeolite, Silicalite, metallosilicate, etc. can use it conveniently.

[0036]A honeycomb structured body may be made to support a catalyst component directly, and an adsorption layer may be made to support it.

[0037]The porosity honeycomb structured body of this invention explained above can be manufactured by the method etc. which are described below.

[0038]2. In the manufacturing method of the porosity honeycomb structured body of manufacturing method this invention of a porosity honeycomb structured body, first, use a cordierite-ized raw material as the main raw material, and produce the Plastic solid of honeycomb structure as ostomy material using the plastic matter which contains carbon at least.

[0039]As a cordierite-ized raw material used for this invention, Usually, source ingredients of silica (SiO_2), such as kaolin, talc, quartz, fused silica, or mullite, What blended source

ingredients of alumina (aluminum$_2O_3$), such as source ingredients of magnesia (MgO), such as talc or magnesite, and kaolin, an aluminum oxide, or aluminium hydroxide, so that it might become the theoretical presentation of a cordierite crystal can be mentioned. However, the thing which shifted the theoretical presentation concerned intentionally depending on the use, or the thing which contained mica, quartz, Fe_2O_3, CaO, Na_2O, or K_2O as an impurity may be used. The porosity and pore diameter of a honeycomb structured body which are obtained may be controlled by controlling the kind or its rate of a compounding ratio of the raw material made to constitute, or controlling about the particle diameter of various raw materials, maintaining the theoretical presentation concerned.

[0040]As carbon made to contain as ostomy material in this invention, graphite, activated carbon, etc. can be mentioned, for example. Graphite can be used as an ostomy agent burned at 600-1200 **, and activated carbon can be used as an ostomy agent burned at 400-1200 **. Carbon is twisted and a plastic matter is made for more than 10 mass % to contain [more than 5 mass % / more than 7 mass %] it preferably especially in this invention.

[0041]Even if it controls the heating rate at the time of calcination as the carbon made to contain as ostomy material is less than 5 mass %, the carbon which exists in the central part of a Plastic solid above 1200 **. Since it becomes difficult for you to make it burned down, or it cannot make the porosity and pore diameter of the honeycomb structured body central part increase from the peripheral part, the problem of producing a calcination piece will be produced.

[0042]However, when performing dielectric drying in the case of a drying process, conductivity is kept from becoming superfluous, and also [required] it is preferred to make carbon contain below by 25 mass % from from, it is more preferred to make it contain below by 23 mass %, and especially the thing made to contain below by 21 mass % is preferred.

[0043]In this invention, other materials may be made to contain as ostomy material, for example, foamed resin, foamed foamed resin, wheat flour, starch, phenol resin, poly methyl methacrylate, polyethylene, or polyethylene terephthalate can be mentioned.

[0044]Especially, foamed foamed resin of an acrylic microcapsule etc. is preferred at the point that the honeycomb structured body of high porosity can be obtained from the start in a small quantity since it is hollow.

[0045]But if the foamed resin burned down by low temperature from carbon is added so much, it will become the environment of temperature up where a stoma is comparatively formed in a low-temperature stage, and carbon burns easily, and control of a heating rate will become difficult. Therefore, as for foamed resin, it is preferred to make it contain by less than 5.0 mass % in a plastic matter, and it is more preferred to make it contain below by 3.0 mass %.

[0046]Other additive agents can be made to contain, for example, a binder, a dispersing agent, etc. may be made to contain in this invention if needed.

[0047]As a binder, for example Hydroxypropylmethylcellulose, Methyl cellulose, hydroxyethyl cellulose, carboxyl methyl cellulose, or polyvinyl alcohol can be mentioned, and ethylene glycol, dextrin, fatty acid soap, or polyalcohol can be mentioned as a dispersing agent, for example.
[0048]According to the purpose, these each additive agent can be independent one sort, or can be combined two or more sorts, and can be used.
[0049]In this invention, although there is no restriction in particular about the manufacturing method of a plastic matter, cordierite-ized raw material 100 mass part is received, for example, It can knead after supplying all the five to ostomy material 40 mass part containing carbon, ten to water 40 mass part, three to binder 5 mass part added if needed, and 0.5 to dispersing agent 2 mass part, and can produce.
[0050]Although an extrusion-molding method, injection molding process, or a press-forming method can be mentioned, for example as a method of producing the Plastic solid of honeycomb structure using the obtained plastic matter, Especially, while continuous molding is easy, it is preferred to carry out by an extrusion-molding method at the point which carries out orientation of the cordierite crystal and is made to low-thermal-expansion nature.
[0051]It is a point which can mention hot air drying, microwave drying, dielectric drying, reduced pressure drying, vacuum drying, or freeze-drying, and can dry the whole promptly and uniformly especially as a drying method of a Plastic solid, for example, It is preferred to carry out by the drying process which combined hot air drying, and microwave drying or dielectric drying.
[0052]Next, in this invention, it is the speed at which the carbon which exists the Plastic solid after desiccation in the central part of the Plastic solid concerned is burned down by not less than 1200 ** less than 1430 ** at Plastic solid central part temperature, and temperature up of the ambient temperature is carried out, and it is calcinated.
[0053]As already stated, the carbon which exists in the central part of a Plastic solid in the heating rate burned down by less than 1200 **. The stoma of a septum [in / in the honeycomb structured body obtained / a concentricity part and the peripheral part] will be an equal diameter, or a calcination piece may be produced and the use as a filter of a honeycomb structured body may become difficult. In the heating rate which is not burned down in addition on the other hand even if the carbon which exists in the central part of a Plastic solid exceeds 1430 **, the blockade of a stoma, the calcination piece of a septum, etc. will be produced in the honeycomb structured body produced by the cordierite which constitutes a septum fusing.
[0054]The carbon which exists in the central part of a Plastic solid here about how the atmosphere heating rate burned down by not less than 1200 ** less than 1430 ** at the temperature of the Plastic solid central part is determined. It is necessary to determine synthetically in consideration of factors, such as a size of the kind of the content of carbon, the

oxygen content of a firing environments, and other ostomy material and content, and a Plastic solid.

[0055]For example, since all the carbon is easily burned down before the temperature of the Plastic solid central part results in 1200 ** when there is little content of carbon, it is necessary to make quick an atmosphere heating rate until the temperature of the Plastic solid central part results in not less than 1200 **. Since similarly destruction by fire of carbon is promoted when increasing the oxygen content of a firing environments, it is necessary to make quick an atmosphere heating rate until the temperature of the Plastic solid central part results in not less than 1200 **.

[0056]Since there are few oxygen supplies in the central part when the slack Plastic solid for calcination is large, it is necessary to make late conversely an atmosphere heating rate until the temperature of the Plastic solid central part results in not less than 1200 **.

[0057]On the other hand, as other ostomy material, when foamed resin is made to contain, for example, Since it is 300-400 ** whose temperature to which the foamed resin concerned is burned down is lower than carbon, in the temperature in which carbon begins to be burned down, the stoma is already formed by destruction by fire of foamed resin, and the environment where destruction by fire of carbon is easy to be promoted is formed. Therefore, it is necessary to make an atmosphere heating rate quick, so that there is much the content, when foamed resin etc. are made to contain as other ostomy material.

[0058]But what is necessary is to choose suitably the atmosphere heating rate in 400-1150 **, and just to usually calcinate it within the limits of 20-60 ** / hr, in consideration of the size of a Plastic solid, the kind of ostomy material, quantity, etc.

[0059]For example, to cordierite-ized raw material 100 mass part, however, activated carbon 10 mass part, Foamed resin 2 mass part using the raw material made to contain 57 to 61% of porosity, When producing the honeycomb structured body of size phi190.5 mmxL203.2 mm-phi 266.7 mmxL305.0mm, it is preferred to calcinate the atmosphere heating rate in 400-1150 ** as 30-35 ** / hr (it is a case where it calcinates with the same heating rate.). When producing the honeycomb structured body of big size phi305.0 mmxL356.0mm, it is preferred to calcinate the atmosphere heating rate in 400-1150 ** as 20-30 ** / hr.

[0060]For example, to cordierite-ized raw material 100 mass part, activated carbon 10 mass part, In producing the honeycomb structured body of 65 to 70% of porosity, and size phi144.0 mmxL152.0mm using the raw material which made 2.2 to foamed resin 2.6 mass part contain, It is preferred to calcinate the atmosphere heating rate in 400-1150 ** as 50-90 ** / hr (it is a case where it calcinates with the same heating rate.). When replacing with activated carbon and using graphite as ostomy material, it is good also as the above-mentioned heating rate at 400-1150 ** ambient temperature, but it can also be considered as the above-mentioned heating rate by 600-1150 ** ambient temperature.

[0061]Change of the porosity from a periphery to an axis direction and a pore diameter can be changed a lot near a periphery by making an atmosphere heating rate quick, and can be changed from a peripheral part to the central part gently-sloping by making an atmosphere heating rate late.

[0062]

[Example]Hereafter, although an example explains this invention concretely, this invention is not limited at all by these examples.

[0063]1. The method shown below about the honeycomb structured body obtained by the example and comparative example which carry out the valuation method after-mentioned estimated.

[0064](1) As shown in pore diameter drawing 2, are perpendicular to the middle point concerned to the septum portion (henceforth the "central part") which approaches most the middle point A or the middle point concerned of the medial axis X of a honeycomb structured body, and is located in it, and a medial axis, About the septum (henceforth a "peripheral part") most located in the peripheral face side B, the pore diameter was measured using the mercury pressure ON type porosimeter made from micro MERITIKKUSU.

[0065](2) About the central part of a porosity honeycomb structured body, and a peripheral part, the total pore volume ratio was measured using the mercury pressure ON type porosimeter made from micro MERITIKKUSU, true specific gravity of cordierite was set to cc in 2.52g /, and porosity was calculated from the total pore volume ratio.

[0066](3) soot catching pressure -- disadvantage -- welding an inside diameter phi215mm ring by pressure to the both-ends side of the honeycomb structured body obtained by each example and a comparative example, and via this ring first, The soot which made it generate with a soot generator was flowed within the limits of phi215.0mm of a honeycomb structured body, and a 33-g soot was made to catch.

[0067]Subsequently, where a soot is caught, the honeycomb structured body passed the air of 6.2 Nm^3/min, and measured the pressure differential before and behind a honeycomb structured body, and the pressure loss in the state where the soot was caught was evaluated.

[0068](4) Whenever [isostatic strong], first, with the metal boards of a honeycomb structured body and an equal diameter, the both ends of the honeycomb structured body were covered, and after fixing metal boards with the rubber tube of a honeycomb structured body and an equal diameter, the elastic tape was stuck on the rubber tube concerned and the outskirts of it, and further, it sealed so that water might not pour in.

[0069]Next, water pressure was increased and the damaged water pressure estimated isostatic intensity (Mpa) until it sank the honeycomb structured body underwater and the honeycomb structured body was damaged in this state.

[0070](5) Where canning of the catalyst body which supported the catalyst to the honeycomb

structured body obtained by pressure loss increasing rate each example and a comparative example is carried out to a metal case, 13-m^3 / min style of the 400 ** air were carried out, the pressure differential before and behind a honeycomb structured body was measured, and this was made into the pressure loss A1. It measured similarly about what is not supporting the catalyst with the same honeycomb structured body, and this was made into the pressure loss A2. 100x(A1-A2)/A2 was calculated and it was considered as the pressure loss increasing rate.

[0071](6) The purification efficiency of HC was evaluated using a 5-l. diesel power plant using the catalyst body by which canning was carried out to the metal case used for the exhaust gas purification efficiency above-mentioned pressure loss measurement. The exhaust gas from an engine was passed to the catalyst body of honeycomb structure, HC concentration B-2 in HC concentration B1 in the exhaust gas before introducing into a catalyst body and the exhaust gas after catalyst body passage was measured, 100x(B1-B-2)/B1 was calculated, and it was considered as exhaust gas purification efficiency.

[0072]2. As shown in No.1 of an example, comparative examples, and those evaluation result (example 1) table 1, Talc (mean particle diameter of 21 micrometers) 39.8 mass %, kaolin (mean particle diameter of 11 micrometers) 18.5 mass %, It mixed at a rate of alumina (mean particle diameter of 7 micrometers) 14.0 mass %, aluminium hydroxide (mean particle diameter of 2 micrometers) 15.2 mass %, and silica (mean particle diameter of 25 micrometers) 12.5 mass %, and the cordierite-ized raw material was adjusted.

[0073]To this cordierite-ized raw material 100 mass part, subsequently, carbon (graphite) (mean particle diameter of 53 micrometers) 10.0 mass part, Foamed resin (mean particle diameter of 50 micrometers) 2.0 mass part, binder 4 mass part, surface-active agent 0.5 mass part, and water 31 mass part were supplied to the kneading machine, it kneaded for 60 minutes, and the plastic matter was obtained.

[0074]Subsequently, the obtained plastic matter was supplied and kneaded to the vacuum kneading machine, the cylinder-like plastic matter was produced, this plastic matter was supplied to the extrusion-molding machine, and it fabricated to honeycomb shape. The bone dry of this Plastic solid was carried out by hot air drying after dielectric drying, and the both-ends side was cut in the predetermined size.

[0075]Subsequently, the breakthrough in the dried body of this honeycomb shape was ****** (ed) in the position from which a breakthrough differs mutually in respect of the both ends which carry out an opening by the slurry which consists of a cordierite-ized raw material of the same presentation.

[0076]At the last, a firing environments to the temperature schedule which makes an oxygen density the range of 10 - 15 volume %, and is shown [in a 600-1150 ** temperature requirement] No.1 of Table 2. It calcinated and the honeycomb structured body (honeycomb

filter) of size:phi229.0 mmxL305.0mm, septum thickness:300micrometer, and cell density:300 cell / inch^2 (46.5x10 $^{-2}$/mm^2) was obtained.

[0077](Example 2) To the temperature schedule shown in No.2 of Table 2, the honeycomb structured body (honeycomb filter) was obtained like Example 1 except having calcinated the Plastic solid.

[0078](Comparative example 1) To the temperature schedule shown in No.3 of Table 2, the honeycomb structured body (honeycomb filter) was obtained like Example 1 except having calcinated the Plastic solid.

[0079](Comparative example 2) As shown in No.2 of Table 1, silica with a mean particle diameter of 35 micrometers was used, To cordierite-ized raw material 100 mass part, and carbon (graphite) 20.0 mass part, Foamed resin 1.5 mass part, binder 4 mass part, surface-active agent 0.5 mass part, and water 34 mass part were supplied to the kneading machine, and the honeycomb structured body (honeycomb filter) was obtained like Example 1 except having kneaded for 60 minutes and having obtained the plastic matter.

[0080](Example 3) As shown in No.2 of Table 1, silica with a mean particle diameter of 35 micrometers was used, To cordierite-ized raw material 100 mass part, and carbon (graphite) 20.0 mass part, To the temperature schedule shown in having supplied foamed resin 1.5 mass part, binder 4 mass part, surface-active agent 0.5 mass part, and water 34 mass part to the kneading machine, having kneaded for 60 minutes, and having obtained the plastic matter, and No.2 of Table 2. The honeycomb structured body (honeycomb filter) was obtained like Example 1 except having calcinated the Plastic solid.

[0081](Comparative example 3) As shown in No.2 of Table 1, silica with a mean particle diameter of 35 micrometers was used, To cordierite-ized raw material 100 mass part, and carbon (graphite) 20.0 mass part, To the temperature schedule shown in having supplied foamed resin 1.5 mass part, binder 4 mass part, surface-active agent 0.5 mass part, and water 34 mass part to the kneading machine, having kneaded for 60 minutes, and having obtained the plastic matter, and No.3 of Table 2. The honeycomb structured body (honeycomb filter) was obtained like Example 1 except having calcinated the Plastic solid.

[0082](Example 4) As shown in No.3 of Table 1, silica with a mean particle diameter of 35 micrometers was used, To cordierite-ized raw material 100 mass part, and carbon (graphite) 5.0 mass part, To the temperature schedule shown in having supplied foamed resin 3.0 mass part, binder 4 mass part, surface-active agent 0.5 mass part, and water 30 mass part to the kneading machine, having kneaded for 60 minutes, and having obtained the plastic matter, and No.4 of Table 2. The honeycomb structured body (honeycomb filter) was obtained like Example 1 except having calcinated the Plastic solid.

[0083](Comparative example 4) As shown in No.3 of Table 1, silica with a mean particle diameter of 35 micrometers was used, To cordierite-ized raw material 100 mass part, and

carbon (graphite) 5.0 mass part, To the temperature schedule shown in having supplied foamed resin 3.0 mass part, binder 4 mass part, surface-active agent 0.5 mass part, and water 30 mass part to the kneading machine, having kneaded for 60 minutes, and having obtained the plastic matter, and No.3 of Table 2. The honeycomb structured body (honeycomb filter) was obtained like Example 1 except having calcinated the Plastic solid.

[0084](Comparative example 5) As shown in No.3 of Table 1, silica with a mean particle diameter of 35 micrometers was used, To cordierite-ized raw material 100 mass part, and carbon (graphite) 5.0 mass part, To the temperature schedule shown in having supplied foamed resin 3.0 mass part, binder 4 mass part, surface-active agent 0.5 mass part, and water 30 mass part to the kneading machine, having kneaded for 60 minutes, and having obtained the plastic matter, and No.1 of Table 2. The honeycomb structured body (honeycomb filter) was obtained like Example 1 except having calcinated the Plastic solid.

[0085]

[Table 1]

調合組成

	コーディエライト化原料(質量%)					カーボン	発泡樹脂	水	バインダー	界面活性剤
No.	タルク	カオリン	アルミナ	水酸化アルミニウム	シリカ	(質量部)	(質量部)	(質量部)	(質量部)	(質量部)
1	39.8(21)	18.5(11)	14.0(7)	15.2(2)	12.5(25)	10.0(53)	2.0(50)	31	4	0.5
2	39.8(21)	18.5(11)	14.0(7)	15.2(2)	12.5(35)	20.0(53)	1.5(50)	34	4	0.5
3	39.8(21)	18.5(11)	14.0(7)	15.2(2)	12.5(35)	5.0(53)	3.0(50)	30	4	0.5

括弧内:平均粒子径(μm)

[0086]

[Table 2]

焼成条件(1)

No.	雰囲気昇温速度(℃/hr)												雰囲気冷却速度(℃/hr)		焼成時間(hr)
	RT~200	~300	~600	~900	~1000	1000	~1150	~1200	~1300	~1400	~1425	1425	~1200	~100	
1	30	4	10	35	35	0	35	5	70	50	20	7	50	200	108.4
2	30	4	10	20	20	0	20	5	70	50	20	7	50	200	120.2
3	30	4	10	20	10	10	50	50	70	50	20	7	50	200	121.7
4	30	4	10	60	60	0	60	5	70	50	20	7	50	200	101.8

[0087](Evaluation result) In addition, although not shown in particular all over Table 3, in each example and a comparative example, it was a range which is satisfactory practically with 95 to 98% about soot collection efficiency.

[0088](1) Examples 1 and 2, comparative example 1 these examples, and a comparative example, All to cordierite-ized raw material 100 mass part Carbon (graphite) 10.0 mass part, It is different using the plastic matter containing foamed resin 2.0 mass part at the point calcinated to the temperature schedule shown in No.1 of Table 2 - 3 in common with the point of having manufactured the honeycomb structured body (honeycomb filter), respectively.

[0089]As shown in Table 3, in Example 1 calcinated with the atmosphere heating rate of 35 ** /

hr, even 600-1150 **. In Example 2 calcinated with the atmosphere heating rate of 20 ** / hr, even 1290 ** (temperature of the Plastic solid central part), and 600-1150 **. The honeycomb structured body was able to be obtained without having burned out all the carbon (graphite) and each producing a calcination piece at not less than 1200 ** less than 1430 **, with 1220 ** (temperature of the Plastic solid central part). The pore diameter and porosity of the central part were all large [the obtained honeycomb structured body] not less than 2% not less than 2 micrometers respectively to the peripheral part. For this reason, although isostatic intensity was as large as 2.9 or more Mpa, soot catching pressure loss was as small as 5.9 or less kpa. The pore diameter and porosity of the central part were [as opposed to / at Example 1 with an especially quick atmosphere heating rate up to 600-1150 ** / the peripheral part] as large as 5 micrometers and 5% respectively, and soot catching pressure loss was also as small as especially 5.2kpa.

[0090]Even 600-900 ** even for 20 ** / hr, and 900-1000 ** On the other hand, 10 ** / hr, In the comparative example 1 calcinated with an atmosphere heating rate which is called maintenance, and which is generally performed at 1000 ** for 10 hours. A calcination piece is accepted in the honeycomb structured body obtained by burning out the carbon of the Plastic solid central part at 1160 ** (temperature of the Plastic solid central part), and practical use cannot be borne as a filter.

[0091]About the honeycomb structured body obtained in Example 1, as shown in drawing 5, the pore diameter and porosity of the septum were perpendicularly measured from the middle point A of the medial axis (center) in the position in every 28.6 mm to the medial axis. As a result, as shown in drawing 6 and drawing 7, porosity and a pore diameter are changing from the peripheral part to the central part continuously.

Even by the septum which forms the cell located in one third from a periphery to a medial axis of length, the whole variation was large 69% 71%, respectively.

[0092](2) Example 3 and the comparative example 2, 3 these examples, and a comparative example, All to cordierite-ized raw material 100 mass part Carbon 20.0 mass part, The plastic matter (it is a plastic matter in which carbon is not burned down easily until it becomes an elevated temperature from the example 1 grade mentioned above.) containing foamed resin 1.5 mass part is used, It is different at the point calcinated to the temperature schedule shown in No.1 of Table 2 - 3 in common with the point of having manufactured the honeycomb structured body (honeycomb filter), respectively.

[0093]As shown in Table 3, in Example 3 calcinated with the atmosphere heating rate of 20 ** / hr, even 600-1150 **. The honeycomb structured body was able to be obtained without having burned down the carbon of the Plastic solid central part, and producing a calcination piece at 1350 ** (temperature of the Plastic solid central part), and not less than 1200 ** less than 1430

**. The obtained honeycomb structured body had [the pore diameter and porosity of the central part] 7 micrometers, and very large 6% and discrepancy to the peripheral part. For this reason, although isostatic intensity was as large as 2.9Mpa, soot catching pressure loss was very as small as 5.0kpa.

[0094]On the other hand, by the comparative example 2 calcinated with the atmosphere heating rate of 35 ** / hr, even 600-1150 **. The honeycomb structured body obtained by burning down the carbon of the Plastic solid central part at the temperature of 1445 ** (temperature of the Plastic solid central part) and not less than 1430 ** which is the melting point of cordierite produces a calcination piece by melting of a septum, and cannot bear practical use as a filter. Even 600-900 ** even for 20 ** / hr, and 900-1000 ** 10 ** / hr, At 1000 **, according to the comparative example 3 calcinated with an atmosphere heating rate which is called maintenance, and which is generally performed conventionally for 10 hours, the carbon of the Plastic solid central part was burned down by 1135 ** (temperature of the Plastic solid central part), and the calcination piece was accepted in the honeycomb structured body obtained too.

[0095](3) Example 4 and the comparative example 4, 5 these examples, and a comparative example, All to cordierite-ized raw material 100 mass part Carbon 5.0 mass part, The plastic matter (it is a plastic matter in which carbon is easilier burned down by low temperature than the example 1 grade mentioned above.) containing foamed resin 3.0 mass part is used, It is different at the point calcinated to the temperature schedule shown in No.1 shown in Table 2, respectively, and 3 and 4 in common with the point of having manufactured the honeycomb structured body (honeycomb filter).

[0096]As shown in Table 3, in Example 4 calcinated with the atmosphere heating rate of 60 ** / hr, even 600-1150 **. The honeycomb structured body was able to be obtained without having burned down the carbon of the Plastic solid central part, and producing a calcination piece at 1285 ** (temperature of the Plastic solid central part), and not less than 1200 ** less than 1430 **. The obtained honeycomb structured body had respectively the pore diameter of the central part and the discrepancy of porosity as large as 3 micrometers and 3% over a peripheral part. for this reason, isostatic intensity -- 2.8Mpa -- practically -- abbreviation -- in spite of having obtained sufficient intensity, soot catching pressure loss was very as small as 5.2kpa.

[0097]Even 600-900 ** even for 20 ** / hr, and 900-1000 ** On the other hand, 10 ** / hr, Before becoming 950 ** (temperature of the Plastic solid central part), and a remarkable temperature requirement of firing shrinkage, carbon ** of the Plastic solid central part was burned down by the comparative example 4 calcinated with an atmosphere heating rate which is called maintenance, and which is generally performed conventionally at 1000 ** for 10 hours. Although the calcination piece was not accepted in the obtained honeycomb structured body, there was no discrepancy about the pore diameter and porosity of a peripheral part and

the central part. For this reason, although the intensity as 2.8Mpa and Example 3 with same isostatic intensity was obtained, soot catching pressure loss became large with 5.9kpa compared with Example 3. In the comparative example 5 which calcinated even 600-1150 ** with the atmosphere heating rate of 35 ** / hr, the calcination piece was accepted in the honeycomb structured body obtained by burning down the carbon of the Plastic solid central part at 1150 ** (temperature of the Plastic solid central part).

[0098]

[Table 3]

実施例と比較例

	調合No.	焼成温度プログラム	グラファイトが燃え尽きた温度	焼成切れ	気孔径(μm)		気孔率(%)		スート捕集圧力損失(Kpa)	アイソスタティック強度(Mpa)
					外周部	中心部	外周部	中心部		
実施例1	1	1	1290	なし	19	24	59	64	5.2	2.9
実施例2	1	2	1220	なし	19	21	59	61	5.9	3
比較例1	1	3	1160	有り	19	20	59	60	—	—
比較例2	2	1	1445	有り	18	—	60	—	—	—
実施例3	2	2	1350	なし	18	25	60	66	5.0	2.9
比較例3	2	3	1135	有り	18	19	60	61	—	—
実施例4	3	4	1285	なし	21	24	61	64	5.2	2.8
比較例4	3	3	950	なし	21	21	61	61	5.9	2.8
比較例5	3	1	1150	有り	21	22	61	62	—	—

[0099](Examples 5-7 and comparative examples 6 and 7) In Example 1, the Plastic solid of the honeycomb shape with which calcination is presented, Respectively phi5.66inchxL6.0inch (phi143.8 mmxL152.4mm), phi7.5 inchxL8.0inch (phi190.5 mmxL203.2mm), phi9.0 inchxL8.0inch (phi228.6 mmxL203.2mm), It produced with the size of phi10.5inchxL12.0inch (phi266.7 mmxL304.8mm) and phi12.0 inchxL14.0inch (phi304.8 mmxL355.6mm), And the honeycomb structured body (honeycomb filter) was manufactured like Example 1 except having calcinated by the temperature program of No.5 shown in Table 4.

[0100]

[Table 4]

焼成条件(2)

No.	雰囲気昇温速度(℃/hr)															雰囲気冷却速度(℃/hr)		焼成時間(hr)
	RT-120	~190	190	~300	~400	~600	~800	~1150	~1200	1200	~1300	~1350	~1400	~1425	1425	1200	100	
5	30	20	12	4	7	10	35	35	5	0	70	70	30	25	7	50	200	127.5
6	30	20	12	4	7	10	30	20	20	2	70	50	50	20	7	50	200	141.0

[0101](Evaluation result) As shown in drawing 3, in the comparative example 6 which calcinated the Plastic solid of size phi5.66inchxL6.0inch (phi143.8 mmxL152.4mm). The peak which shows that the carbon of the Plastic solid central part was burned down at 1080 ** (temperature of the Plastic solid central part) which is a big temperature requirement of firing shrinkage was accepted. In the comparative example 7 which calcinated the size phi12.0inchxL14.0inch (phi304.8 mmxL355.6mm) Plastic solid, the peak which shows that the carbon of the Plastic solid central part was burned down was accepted at the time of about

1310 ** (temperature of the Plastic solid central part).
[0102]A size, respectively On the other hand, phi7.5 inchxL8.0inch (phi190.5 mmxL203.2mm), phi9.0 inchxL8.0inch (phi228.6 mmxL203.2mm), In Examples 5-7 which are phi10.5 inchxL12.0inches (phi266.7 mmxL304.8mm). The peak which all indicates it that the carbon of the Plastic solid central part was burned down to be 1220 **, 1250 **, and 1290 ** (all are the temperature of the Plastic solid central part) at not less than 1200 ** less than 1430 **, respectively was accepted.
[0103](Example 8 and the comparative examples 8-10) In Example 1, the Plastic solid of the honeycomb shape with which calcination is presented, Respectively phi5.66inchxL6.0inch (phi143.8 mmxL152.4mm), phi7.5 inchxL8.0inch (phi190.5 mmxL203.2mm), It produced with the size of phi9.0inchxL8.0inch (phi228.6 mmxL203.2mm) and phi10.5 inchxL12.0inch (phi266.7 mmxL304.8mm), And the honeycomb structured body (honeycomb filter) was manufactured like Example 1 except having calcinated by the temperature program of No.6 shown in Table 4.
[0104](Evaluation result) As shown in drawing 4, a ******** size phi7.5 inchxL8.0inch (phi190.5 mmxL203.2mm), In the comparative examples 9 and 10 which calcinated the Plastic solid of phi9.0 inchxL8.0inch (phi228.6 mmxL203.2mm). The peak which shows that the carbon of the Plastic solid central part was burned down at 1130 ** which is a big temperature requirement of firing shrinkage, and 1190 ** (all are the temperature of the Plastic solid central part), respectively was accepted. In the comparative example 8 whose size is phi5.66inchxL6.0inch (phi143.8 mmxL152.4mm), the peak which shows that the carbon of the Plastic solid central part was burned down at 990 ** (temperature of the Plastic solid central part) was accepted.
[0105]On the other hand, in Example 8 whose size is phi10.5 inchxL12.0inch (phi266.7 mmxL304.8mm), the peak which shows that the carbon of the Plastic solid central part was burned down at 1310 ** (temperature of the Plastic solid central part) and not less than 1200 ** less than 1430 ** was accepted.
[0106](Example 9) In Example 1, the honeycomb structured body (catalyst support) of size:phi229.0 mmxL152.0mm, septum thickness:300micrometer, and cell density:300 cell / $inch^2$ was manufactured like Example 1 except not having performed the process of ******(ing) a breakthrough. When high specific surface area alumina and 500g of platinum system oxidation catalysts were supported to each obtained honeycomb structured body and it was made it with the catalyst body, the pore diameters of the peripheral part of a catalyst body and the central part were 14 micrometers and 19 micrometers, respectively, and the porosity of the peripheral part of a catalyst body and the central part was 54% and 59%, respectively.
[0107](Comparative example 11) In the comparative example 4, the honeycomb structured body (catalyst support) of size:phi229.0 mmxL152.0mm, septum thickness:300micrometer, and cell density:300 cell / $inch^2$ was manufactured like Example 4 except not having performed

the process of ******(ing) a breakthrough. When high specific surface area alumina and 500g of platinum system oxidation catalysts were supported to each obtained honeycomb structured body and it was made it with the catalyst body, the pore diameters of the peripheral part of a catalyst body and the central part were 15 micrometers and 15 micrometers, respectively, and the porosity of the peripheral part of a catalyst body and the central part was 55% and 55%, respectively.

[0108](Evaluation result) As shown in Table 5, the porosity and pore diameter in the central part, By 4 micrometers and the catalyst body using the honeycomb structured body of big Example 9, the isostatic intensity after catalyst support became large with 5.8Mpa 4% from the porosity and pore diameter in the peripheral part according to increase of the catalyst holding amount by a raise in porosity, and major-diameter-izing, respectively. And the pressure loss increasing rate was as small as 5%, and exhaust gas purification efficiency was as large as 70%.

[0109]On the other hand, in the catalyst body using the honeycomb structured body of the same comparative example 11 as the porosity and pore diameter in the peripheral part, the isostatic intensity after catalyst support had the small porosity and pore diameter in the central part compared with 5.5Mpa and the honeycomb structured body of Example 9. The pressure loss increasing rate was also large compared with the honeycomb structured body of 11% and Example 9, and exhaust gas purification efficiency was small compared with the honeycomb structured body of 58% and Example 9.

[0110]

[Table 5]

	調合No.	焼成温度プログラム	グラファイトが燃え尽きた温度	焼成切れ	気孔径*1(μm)		気孔率*1(%)		圧力損失上昇率(%)	排ガス浄化効率(%)	アイソスタティック強度(Mpa)
					外周部	中心部	外周部	中心部			
実施例9	1	1	1270	なし	14	19	54	59	5	70	5.8
比較例11	3	3	910	なし	15	15	55	55	11	58	5.5

*1気孔率、気孔径とも触媒担持後の値を示す。

[0111]

[Effect of the Invention]As explained above, according to this invention, pressure loss and the opposite characteristic of isostatic intensity can be satisfied simultaneously, A suitable porosity honeycomb structured body for the catalyst support which supports the filter which carries out catching removal of the particulate matter in exhaust gas especially, and the catalyst which decomposes NOx in exhaust gas and HC and is removed, and a manufacturing method for the same can be provided.

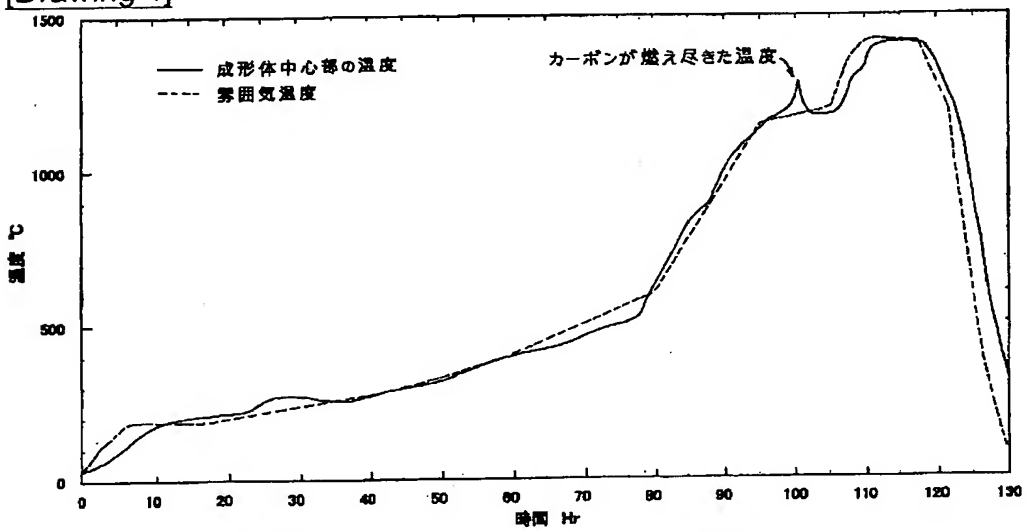
[Translation done.]

* NOTICES *

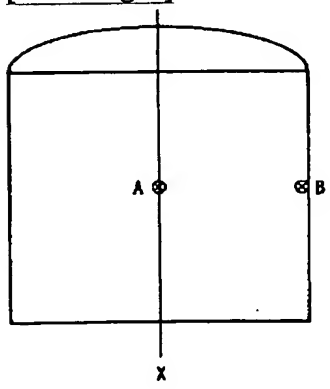
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

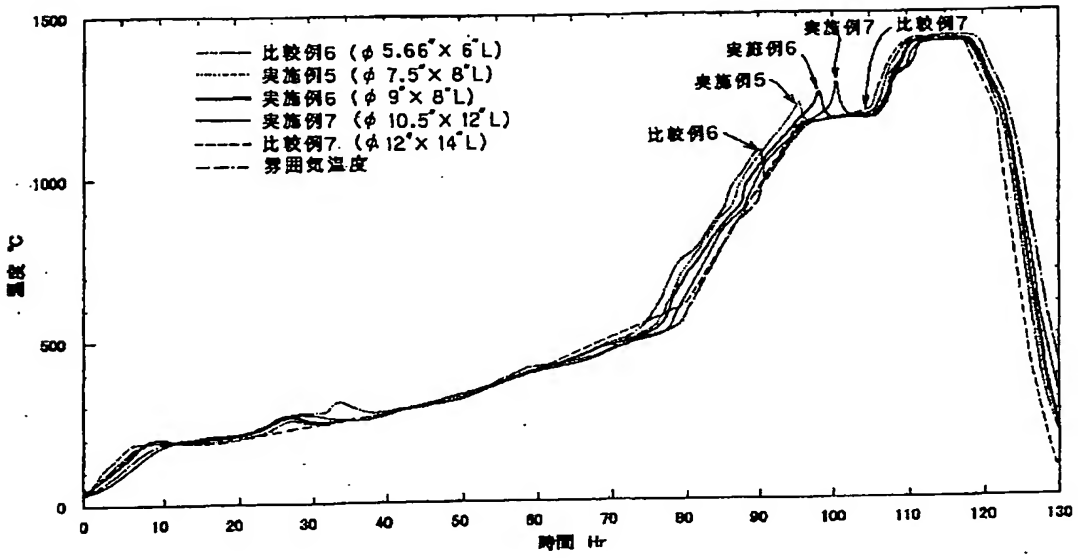
[Drawing 1]



[Drawing 2]



[Drawing 3]



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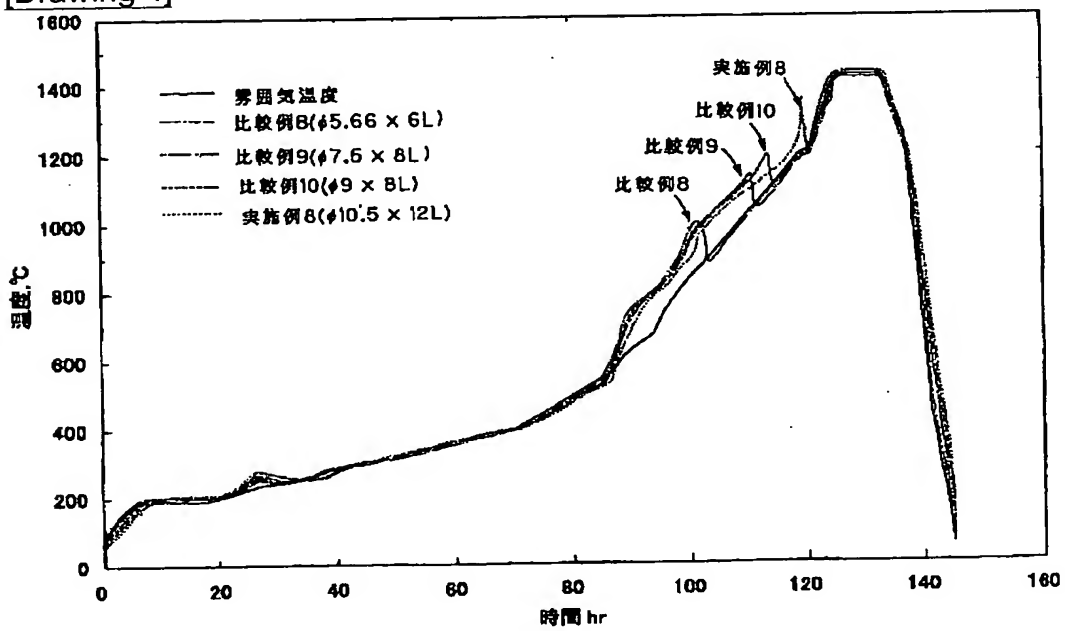

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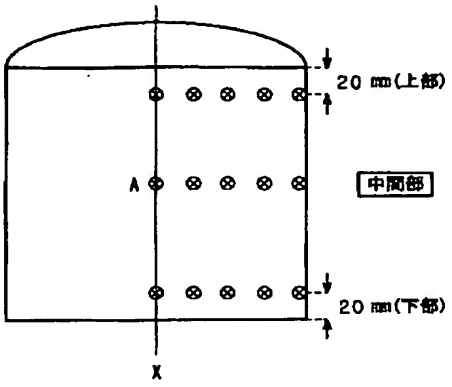

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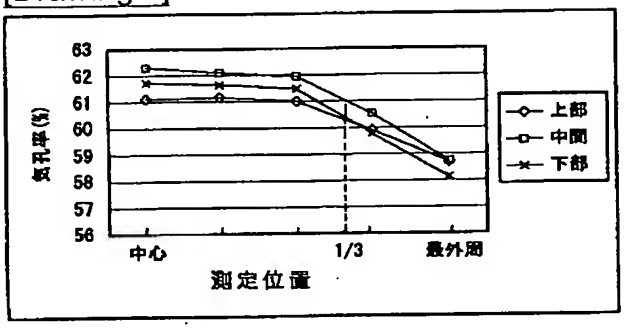

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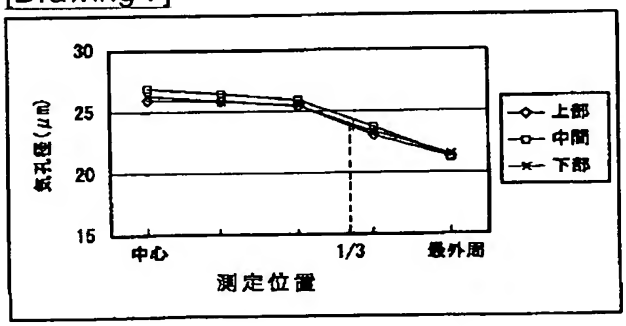

[Translation done.]

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最終頁に続く

(54)【発明の名称】　多孔質ハニカム構造体、その用途及びその製造方法

(57)【要約】
【課題】　圧力損失と、アイソスタティック強度という相反する特性を同時に満足させることができる多孔質ハニカム構造体及びその製造方法を提供する。
【解決手段】　コーディエライトを主結晶相とする気孔率４０～７５％、かつ平均気孔径１０～５０μｍの隔壁を備える多孔質ハニカム構造体において、同中心部における気孔率及び気孔径を、同外周部における気孔率及び気孔径より大きなものとする。

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【特許請求の範囲】

【請求項１】　コーディエライトを主結晶相とする気孔率４０～７５%、かつ平均気孔径１０～５０μmの隔壁を備える多孔質ハニカム構造体であって、
該ハニカム構造体の中心部における気孔率及び気孔径が、同外周部における気孔率及び気孔径より大きいことを特徴とする多孔質ハニカム構造体。

【請求項２】　前記ハニカム構造体の中心部における気孔率が、前記同外周部における気孔率に対して、２%以上大きく、かつ該ハニカム構造体の中心部における気孔径が、該同外周部における気孔径に対して、２μm以上大きい請求項１に記載の多孔質ハニカム構造体。

【請求項３】　前記ハニカム構造体の中心部における気孔率が、前記同外周部における気孔率に対して、３%以上大きい請求項１又は２に記載の多孔質ハニカム構造体。

【請求項４】　該ハニカム構造体の中心部における気孔径が、該同外周部における気孔径に対して、３μm以上大きい請求項１～３の何れか一項に記載の多孔質ハニカム構造体。

【請求項５】　請求項１～４の何れか一項に記載の多孔質ハニカム構造体のフィルター又は触媒担体としての使用方法。

【請求項６】　コーディエライト化原料を主原料とし、少なくともカーボンを、該コーディエライト化原料１００質量部に対して５質量部以上含有する坏土を用いてハニカム構造の成形体を作製し、該成形体を、乾燥、焼成する多孔質ハニカム構造体の製造方法であって、
該成形体を焼成する際に、雰囲気温度を、該成形体の中心部に存在するカーボンが、成形体中心部温度１２００℃以上１４３０℃未満で焼失する速度で昇温することを特徴とする多孔質ハニカム構造体の製造方法。

【請求項７】　前記雰囲気温度を、４００～１１５０℃の温度範囲で、２０～６０℃／ｈｒの速度で昇温する請求項６に記載の多孔質ハニカム構造体の製造方法。

【請求項８】　前記雰囲気温度を、１１５０～１２００℃の温度範囲で、５時間以上、同温度範囲内に保持する請求項６又は７に記載の多孔質ハニカム構造体の製造方法。

【請求項９】　前記カーボンを、前記コーディエライト化原料１００質量部に対して、２５質量部以下で含有する坏土を用いる請求項６～８の何れか一項に記載の多孔質ハニカム構造体の製造方法。

【請求項１０】　前記成形体を焼成する際の雰囲気が、４００～１１５０℃の雰囲気温度で、酸素濃度７～１７体積%である請求項６～９の何れか一項に記載の多孔質ハニカム構造体の製造方法。

【請求項１１】　更に、発泡樹脂を、前記コーディエライト化原料１００質量部に対して、５質量部未満で含有する坏土を用いる請求項６～１０の何れか一項に記載の

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多孔質ハニカム構造体の製造方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】　本発明は、多孔質ハニカム構造体、その用途及びその製造方法に関する。さらに詳しくは、気孔率及び気孔径の分布を制御して、アイソスタティック強度を維持しながら、圧力損失を低減した多孔質ハニカム構造体及びその製造方法に関する。なお、本発明の多孔質ハニカム構造体は、特に、排ガス浄化用のフィルターや、触媒担体として好ましく用いることができる。

【０００２】

【従来の技術】　自動車用エンジン、特に、ディーゼルエンジン等から排出される粒子状物質やＮＯｘの環境への影響が最近大きくクローズアップされてきており、このような有害物質を除去する重要な手段として、多孔質ハニカム構造体の利用が種々検討されている。

【０００３】　例えば、多孔質の隔壁により仕切られた複数の貫通孔を有するハニカム構造体において、貫通孔が開孔する両端面で互いに異なる位置で目封じした構造とし、一の端面に開口する各貫通孔に排ガスを流入させて、強制的にハニカム構造体内の隔壁を通過させることにより、排ガス中の粒子状物質を捕集、除去するハニカムフィルターが開発されている。また、触媒担持量を増大させることにより、浄化性能を向上させる新たな試みとして、全隔壁を高気孔率の多孔質体として、ＨＣやＮＯｘを分解する触媒を担持させたハニカム構造の触媒体も開発が進められている。

【０００４】　一方、このような多孔質ハニカム構造体は、使用の際に、金属ケース等に把持材を介して把持されるが、エンジン等からの継続的な振動を受けても金属ケースとハニカム構造体にずれが起こらないよう一定の押圧力で把持するため、これに耐え得るアイソスタティック強度が要求される。特に、近年にあっては、低燃費、高出力化といった点からの圧力損失低減の要請、或いは排ガス浄化性能の向上といった点からの触媒担持量増大の要請から、ハニカム構造体の高気孔率化が進展しており、この高気孔率化の要請を満たしながら充分なアイソスタティック強度を確保する必要性が強く指摘されている。また、排ガス経路に設置される多孔質ハニカム構造体にあっては、排ガスの流量が、流路の中央部分で多くなり、当該ハニカム構造体の中央部分での排ガスの流れ易さやＨＣやＮＯｘ分解量が、全体の圧力損失や浄化性能に大きく影響することから、このような排ガスの流量分布の相違に的確に対応した構造のフィルター及び触媒体が望まれている。

【０００５】　これに対して、従来の多孔質ハニカム構造体としては、「その気孔率が４５%以上６０%以下であり、その孔径１００μm以上の気孔容積が全気孔容積の１０%以下であり、その表面から内部に向かって開口